

SPECIFICATION

**JEFFREY B. MUSAT
DAVID C. MEISSNER
ASHVIN SRIVASTAVA
JEFFREY K. CHEETHAM
ABID BENGALI**

**METHOD OF MAKING AN INERT ANODE FOR
ELECTROLYTIC REDUCTION OF METAL OXIDES**

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our co-pending U. S. Patent Application Serial No. 10/641,635, filed August 15, 2003, and also claims the benefit of U.S. Provisional Patent Application Serial No. 60/420,240, filed October 22, 2002.

5

FIELD OF THE INVENTION

The present invention relates to a method and apparatus for producing an inert anode for metal oxide electrolytic reduction, and more particularly relates to a means for protecting an anode from attack by the electrolyte and liberated oxygen during the electrolysis of alumina to aluminum.

BACKGROUND OF THE INVENTION

Since the advent of the electrolytic reduction process for producing aluminum, the anodes used have been made of carbon which is consumed during the electrolytic reduction process. In the more recent past (20 years) there has been an effort to produce an inert anode or electrode that is not consumed during reduction. Metal anodes, ceramic anodes, and cermet anodes have been proposed for development. Metal anodes are currently being developed in addition to the development work being conducted on cermet anodes of the electrolyte cell, which generally operates at a temperature of about 950°C. Metal anodes are attacked by the cryolite electrolyte and by the oxygen evolved at the anode. The current development effort is focused on developing coatings to protect the metal anode or at least to slow down the rate of attack to manageable levels. Metal oxide coatings have been proposed. These coatings are applied to the metal anode by metal oxide slurry addition, by plasma spray coating of a metal oxide or metal followed by an oxidation step, or by the self-forming of an oxide of the actual anode metal during electrolysis. The oxide coatings formed tend to be somewhat porous to the oxygen evolved at the anode, which then continues to attack or oxidize the metal substrate of the anode. This attack or oxidation reduces the life of the anode. Some of the coatings applied may be applied in multiple layers, which in turn requires complex and costly processing steps.

DESCRIPTION OF THE PRIOR ART

Applicant is aware of the following U. S. Patents concerning non-carbon, metal based anodes for electrolytic reduction of aluminum:

	<u>US Patent No.</u>	<u>Inventor</u>	<u>Title</u>
5	6,436,274	DeNora et al.	SLOW CONSUMABLE NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS
10	6,379,526	DeNora et al.	NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS
15	6,372,099	Duruz et al.	CELLS FOR THE ELECTROWINNING OF ALUMINUM HAVING DIMENSIONALLY STABLE METAL-BASED ANODES
	6,361,681	DeNora et al.	SLURRY FOR COATING NON-CARBON METAL-BASED ANODES FOR METAL PRODUCTION CELLS
20	6,248,227	DeNora et al.	SLOW CONSUMABLE NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS
25	6,113,758	DeNora et al.	POROUS NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS
	6,103,090	DeNora et al.	ELECTROCATALYTICALLY ACTIVE NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS

<u>US Patent No.</u>	<u>Inventor</u>	<u>Title</u>
6,077,415	Duruz et al.	MULTI-LAYER NON-CARBON METAL-BASED ANODES FOR ALUMINUM PRODUCTION CELLS AND METHOD
5,904,828	Sekhar et al.	STABLE ANODES FOR ALUMINUM PRODUCTION CELLS
5,510,008	Sekhar et al.	STABLE ANODES FOR ALUMINUM PRODUCTION CELLS

SUMMARY OF THE INVENTION

The invention provides a method for producing a non-carbon inert anode for metal oxide electrolytic reduction, such as reduction of aluminum, by feeding metallic iron and metallic nickel in solid form to an oxidizing reactor; oxidizing the iron and nickel and forming molten nickel ferrite; then coating an anode substrate with a thin coating of the molten ferrite, or other desired molten oxide coating. Molten nickel ferrite can be also formed by melting solid nickel ferrite or by melting oxides of iron and nickel. Metal containing compounds, especially oxides, may be added to dope the ferrite, which increases the electrical conductivity of the ferrite.

The inert anode has a ceramic portion, which is solidified from a molten metal oxide bath and a substrate onto which the ceramic portion is solidified. The ceramic portion may also include a metal component that is dispersed into the ceramic bath prior to solidification.

The ceramic material is coated onto a separately fabricated substrate to form an inert anode. The substrate can be a metal, cermet, or ceramic material. Use of this method is simpler and more cost efficient than the current state of the art of inert metal anode manufacture.

5 The invention also comprises apparatus for producing an inert anode for metal oxide electrolytic reduction, the apparatus comprising: an oxidizing reactor; means for feeding metallic iron and metallic nickel to the oxidizing reactor; a ladle or tundish positioned for receiving molten metal oxide from the reactor; and means for discharging molten metal oxide from the ladle or tundish onto the substrate by spray atomization, by pouring over the substrate, or by discharging into a vessel into which the substrate may be dipped into the
10 molten metal oxide. The substrate is advantageously cooled during dipping or spray coating to keep the substrate from melting. Suitable cooling is effected by water cooling or by air being blown against the substrate.

15 The invention also comprises the product of the method, a non-carbon, inert, metal-based anode for metal oxide electrolytic reduction comprising a nickel ferrite coating on a metal, cermet or ceramic substrate.

OBJECTS OF THE INVENTION

20 The principal object of the present invention is to provide a process for the manufacture of inert anodes that is simpler and more cost efficient than the current state of the art of metal based anode manufacture.

Another object of the invention is to produce an inert anode that has as good or better properties of conductivity, strength, resistance to attack by electrolyte and oxygen in a metal oxide reduction process than metal based anodes.

5 Another object of the invention is to provide an inert anode for electrolytic reduction of metal oxides.

A further object of this invention is to provide apparatus for the manufacture of ceramic coated inert anodes.

10 Another object of this invention is to provide a ceramic type inert anode made from a ferrite that may be used as an anode in the brine electrolysis process in the chlor-alkali industry.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects will become more readily apparent by referring to the following detailed description and the appended drawings in which:

15 Figure 1 is a cross-section of an inert anode produced according to the invention.

Figure 2 is a cross-section of an alternative inert anode according to the invention.

Figure 3 is a cross-section of another alternative inert anode according to the invention.

Figure 4 is a cross-section of a further alternative inert anode, having a generally metal substrate according to the invention.

5 Figure 5 is a schematic diagram of the method and apparatus of a preferred embodiment of the invention.

Figure 6 is a schematic diagram of the method and apparatus of another alternative embodiment of the invention which utilizes a melting furnace rather than an oxidizing furnace.

10 Figure 7 is a schematic diagram of an alternative embodiment of the invention utilizing a variation of feed materials to the oxidizing furnace.

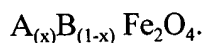
Figure 8 is a schematic diagram of an alternative embodiment of the invention utilizing spray coating of the anode substrate.

Figure 9 is a plan view of an alternative substrate having a grid configuration.

15 Figure 10 is an elevation view of the substrate of Figure 9.

DETAILED DESCRIPTION

In the invented process, a molten metal oxide compound is formed by melting oxides or by oxidizing iron and other metal(s) to form a molten ferrite of the general formula



5 where A & B are divalent metal ions such as Mg, Ni, Mn, Co, Fe; and x can vary from 0 to 1.0.

Alternatively, the molten oxide can be formed by any desired combination of melting and oxidation. The molten oxide is then applied to the substrate of the anode. This can be achieved by dipping the anode substrate into the molten oxide, or by pouring the molten oxide
10 in a controlled manner over the surface of the anode substrate, or by spray atomizing of the molten oxide onto the surface of the substrate. The surface of the substrate may have a raised and/or dimpled or knurled surface to aid in the adherence of the molten coating on the metal substrate. The metal surface of the anode substrate may also be oxidized to aid in the adherence of the molten coating. This oxide layer or coating acts as a controlled interfacial
15 layer assisting in bonding the molten oxide to the substrate. Varying time, temperature and oxygen content of the oxidizing atmosphere will control the thickness of the oxide layer or coating. The substrate may be cooled during dipping or spray coating to keep the substrate from melting. After the molten coating is applied, the coated anode is allowed to cool in a controlled manner to avoid delaminating of the coating from the substrate and/or formation of
20 cracks in the coating.

In a preferred embodiment, metallic iron and metallic nickel in briquet form are fed to an oxidizing reactor where the iron and nickel are melted and oxidized by oxygen. The iron and nickel are fed into the reactor in a molar ratio of

$$\text{Fe/Ni} = 2/1 .$$

5 A molten nickel ferrite of formula $\text{Ni Fe}_2\text{O}_4$ is formed.

It is also possible to utilize a molar ratio of Fe/Ni of greater than 2/1 to produce a mixture of nickel ferrite ($\text{Ni Fe}_2\text{O}_4$) and iron ferrite (Fe_3O_4). It is also possible to operate with a molar ratio of Fe/Ni less than 2 in order to produce a nickel ferrite plus excess nickel oxide (NiO).

10 The molten nickel ferrite is discharged from the oxidizing reactor at a temperature of at least 1660°C, which is sufficient to maintain it in the molten state. The molten nickel ferrite is discharged into a holding vessel such as a ladle or hearth, wherein it forms a molten bath. The ladle can be heated to prevent the molten mixture from solidifying. Dopants may be added to the ladle. Suitable dopants include zinc, cobalt, or lithium compounds, which are
15 preferably added as oxides. Alternatively, dopants can be added in metal sulfide or carbonate form, but they will be present in the final product as oxides. The metal substrate is dipped into the bath and coated with the molten nickel ferrite. The substrate may be repeatedly dipped into the molten bath to increase and control the thickness and other properties of the coating. An electrical connector can be affixed to the anode before or after coating. The
20 finished product is a coated inert anode of correct shape with an electrical connector attached.

The connector can be any desired electrically conductive material, such as copper, nickel, or nickel-iron.

As shown in Figure 1, the product is an inert anode 10 having a substrate 12, an electrical connector 14 affixed thereto, and a coating of nickel ferrite 16 thereon.

5 The coated anode of Figure 2 has a hollow configuration, the substrate 12a preferably being cylindrical and closed at the bottom to form recess 30 therein. The coating 16 may be applied by dipping or spraying. An electrical connector can be affixed to the substrate, such as by welding.

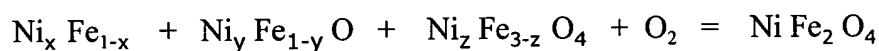
10 The anode 10 of Figure 3 has wires or rods 18 of the same material as the substrate depending therefrom to promote adherence of the coating material 16. Alternatively, the wires or rods can be any material from which the substrate can be made, as described above.

15 Figure 4 shows a metal wire substrate, the wires 20 forming the substrate, the wires also forming the conductor at their upper ends 22. The upper ends of the wires may be connected to a terminal head by swaging and / or soldering. A guide block 24 may be provided to space the wires which depend downwardly therethrough prior to dipping them into a metal oxide bath. A gap 26 is shown between the guide block and the coating 16, but in practice there is little or no gap. The wires, which are preferably copper, comprise about

five to twenty-five percent (5 - 25%) of the finished anode by weight, preferably about ten to twenty percent (10 - 20%).

The electrical connector 20 is preferably an INCONEL rod embedded in or connected to the substrate. Alternatively the connector can be another conductive metal or alloy, or it can be the same composition as the substrate, as described above.

After coating and cooling, the anode may be post-heat treated. This treatment may be an annealing step carried out in an oxygen-containing atmosphere. This post heat treatment is for stress relief, phase composition adjustment, as required, and final microstructure adjustment. The post heat-treatment step may include a soak at a temperature of from 1000°C to 1400°C in an oxygen-containing gas to further oxidize any remaining metallic nickel and metallic iron. This first soak may then be followed by a slow cooling to a reduced temperature 100 to 400°C less than the temperature of the first soak, and then a second soak in an oxygen-containing gas at the reduced temperature. The second soak causes phase composition adjustment and microstructure adjustment. The overall reaction taking place in the post-heat treatment step may be represented by the following reaction:



An alternative post treatment is, after the slow cooling, or after the second soak, hot isostatic pressing of the coated anode at a temperature of at least 1000°C and a pressure of at least 1360 bar for a period of from about 4 to about 8 hours.

In a preferred embodiment shown in Figure 5, metallic iron and metallic nickel in briquet form from source 40 are fed to an oxidizing reactor 42 wherein the iron and nickel are melted and oxidized by oxygen from source 44. The iron and nickel are fed into the reactor in a molar ratio of

5
$$\text{Fe/Ni} = 2/1 .$$

A molten nickel ferrite of formula $\text{Ni Fe}_2\text{O}_4$ is formed.

It is possible to utilize a molar ratio of Fe/Ni greater than 2/1 to produce a mixture of nickel ferrite ($\text{Ni Fe}_2\text{O}_4$) and iron ferrite (Fe_3O_4). It is also possible to operate with a molar ratio of Fe/Ni less than 2 in order to produce a nickel ferrite plus excess nickel oxide (NiO).

10 The molten nickel ferrite is discharged from the oxidizing reactor 42 through outlet 46 at a temperature sufficient to maintain it in the molten state plus sufficient superheat to melt any dopants being added thereto. The molten nickel ferrite discharges into a receiving and holding vessel 48 such as a tundish or ladle. Dopants 50, such as zinc oxide, cobalt oxide, or lithium oxide, can be added and mixed into the molten nickel ferrite in the holding vessel

15 wherein the dopants are melted. The molten oxide may be stirred with an oxygen containing gas 52 through inlet 54 or through injector 56, and any remaining metal is oxidized. The dopant that is added can be in the form of powder or larger particles that are readily melted. The ladle or tundish 48 can be heated to prevent the molten metal oxide compound from solidifying. The molten compound is discharged from the tundish 48 into a molten bath

20 container for coating of substrate 12. A substrate is dipped in the molten bath to form a

coated anode. The substrate is advantageously cooled, as shown by injecting cooling water into the interior 30 of by the substrate. Alternatively, the substrate can be cooled by forced air cooling.

It is also to be understood that a ceramic-coated inert anode made in accordance with the disclosed process may be used in other electrolytic reduction processes besides aluminum such as magnesium, lithium, or calcium reduction.

ALTERNATIVE EMBODIMENTS

The substrate 12 may be metal, cermet or a ceramic. If metal, it may be a solid unit, or it may incorporate multiple rods 18 (Figure 3) or wires 20 (Figure 4), which may be embedded therein and depend downwardly therefrom. The coating 16 adheres to and surrounds these rods or wires, which promote cooling of the coating. The substrate may have a raised surface, or raised portions, such as a waffle pattern, knurls, or dimples which may be raised or indented. The substrate may be oxidized, if desired. All of these promote adherence of the coating to the substrate.

The coating may be a ceramic, or a combination of a ceramic and dispersed metal. The ceramic may be a metal oxide, preferably NiFe_2O_4 , but can be a ferrite of nickel, manganese, magnesium, cobalt, aluminum, or a combination thereof.

If the substrate is a ceramic or a cermet, the coating is generally thicker than if the substrate is metal.

5 The metal substrate could be a bi-metallic material, the metals having different coefficients of expansion. The coefficient of expansion of the metal surface on which the coating is to be applied is matched closely to that of the coating material. Suitable bi-metallics include: iron-nickel-chromium alloy and nickel; and an iron base metal and nickel or nickel alloy.

The molten ceramic bath can be formed by melting oxides of metal in a gas fired furnace, an electric furnace or a combination gas/electric furnace.

10 It is also to be understood that the invented inert anode made from a ferrite may be used in other electrolytic reduction processes besides aluminum, such as electrolytic reduction of magnesium, lithium, or calcium. It is also understood that a ceramic type inert anode made from a ferrite may be used as an anode in the brine electrolysis process in the chlor-alkali industry.

15 Thickness of the coating on the substrate can be controlled by repeating the selected process technique until the desired coating is obtained.

In the alternative embodiment shown in Figure 6, solid nickel ferrite 70, or a mixture of nickel ferrite, nickel oxide and iron oxide (or hematite), or iron-containing and nickel-containing compounds 72 are melted in a melting furnace or vessel 74, which need not be an oxidizing vessel, to form molten nickel ferrite. The melting vessel can be a gas fired furnace, induction furnace, or electric arc furnace.

In the alternative embodiment shown in Figure 7, mostly metallic iron and nickel 40 are fed to reactor 82 along with some iron oxide and/or nickel oxide, which are melted and oxidized to form molten nickel ferrite. There is sufficient exothermic heat available from the oxidation of nickel and iron to allow the use of nickel oxide and iron oxide as feed materials to the reactor. The molten nickel ferrite is then discharged into a ladle or tundish and further treated, then discharged into a container into which a substrate is dipped to form a coated anode. The substrate is advantageously cooled by injecting cooling water into the substrate. Alternatively, the substrate can be cooled by forced air cooling, i.e., blowing of air onto the substrate. In this embodiment, solid nickel oxide 84, or iron oxide 86, or a mixture of nickel oxide and iron oxide 88 is introduced to and melted in an oxidizing reactor or vessel 82, to form molten nickel ferrite. Spent anodes may be utilized as part of the oxide feed material.

In the alternative embodiment of Figure 8, metallic iron and metallic nickel from source 40 are fed to oxidizing reactor 42 wherein the iron and nickel are melted and oxidized by oxygen from source 44. The molten nickel ferrite is discharged from the oxidizing reactor 42 into a receiving and holding vessel 48 such as a tundish or ladle. Dopants can be added

and mixed into the molten nickel ferrite in the holding vessel 48. The molten oxide compound is discharged into a container and atomized in a spray atomizer 66, then sprayed onto the substrate to form a coated anode 10. It is advantageous to cool the substrate while the coating is being applied.

5 In a further alternative substrate shown in Figures 9 and 10, the substrate is a grid 90 of rods 92, 94, which are fixed into position, preferably by welding. A connector can be welded to the rod grid prior to coating of the substrate with the molten oxide compound. This type of substrate can be coated by dipping or spraying.

SUMMARY OF THE ACHIEVEMENT OF THE OBJECTS OF THE INVENTION

10 From the foregoing, it is readily apparent that we have invented an improved process for the manufacture of inert anodes for electrolytic reduction of metal oxides that is simpler and more cost efficient than the current state of the art of anode manufacture, an anode product that has as good or better properties of conductivity, strength, resistance to attack by the electrolyte than metal based anodes, and apparatus for the manufacture of inert anodes.

15 It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the spirit and scope of this invention, which is therefore understood to be limited only by the scope of the appended claims.